

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

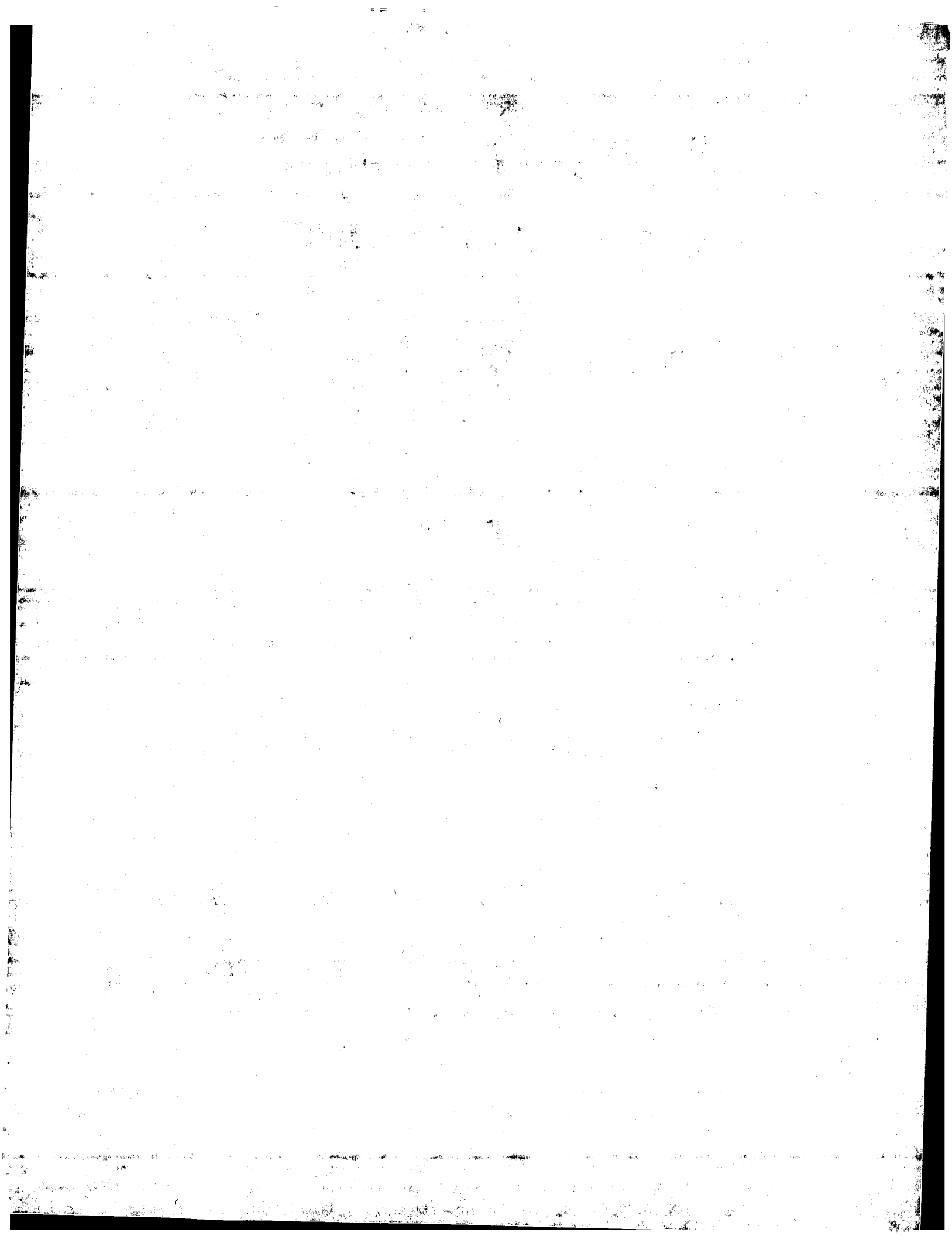
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

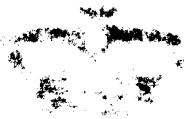
**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



09 914 699  
03-27 04

**APPENDIX B**  
**PRIORITY DOCUMENT**



MEMORANDUM

TO : DIRECTOR, FBI

FROM : SAC, [illegible]



INVESTOR IN PEOPLE



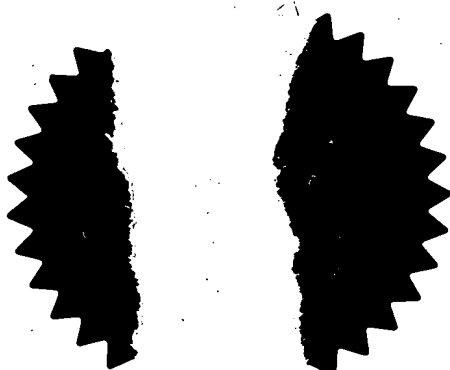
The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

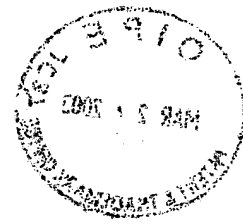
In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed *Stephen Hendley*  
Dated 13 March 2003



Handwritten signature: *John H. ...*

**Patent Form 1/77**

Patents Act 1977  
(Rule 16)



04MAR99 E430018-1 0028/7  
P01/7700 0.00 - 9904926.4

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

**Request for grant of a patent**

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference

HL71375/JDMA

2. Patent application number

(The Patent Office will fill in this part)

04 MAR 1999

**9904926.4**

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Thomas Swan & Co. Ltd.  
Crookhall  
Consett  
Co. Durham DH8 7ND

Degussa Huls AG  
Rodenbacher Chaussee 4  
D-63457 Hanau

Patents ADP number (*if you know it*)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

Germany

4. Title of the invention

Acid-Catalysed Reactions

5. Full name of your agent (*if you have one*)

Haseltine Lake & Co.

"Address for service" in the United Kingdom to which all correspondence should be sent (*including the postcode*)

Imperial House  
15-19 Kingsway  
London WC2B 6UD

Patents ADP number (*if you know it*)

34001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (*if you know it*) the or each application number

Country

Priority application number  
(*if you know it*)

Date of filing  
(*day/month/year*)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(*day/month/year*)

8. Is a statement of inventorship and of right to a grant of patent required in support of this request? (*Answer "Yes" if:*

YES

- a) any applicant named in part 3 is not an inventor, or  
b) there is an inventor who is not named as an applicant, or  
c) any named applicant is a corporate body.  
See note (d))

**Patents Form 1/77**

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

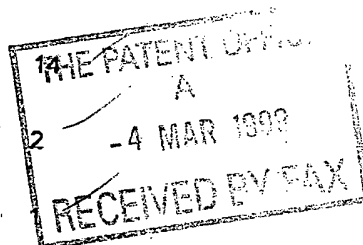
Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)



10. If you are also filing any of the following,

Priority documents

Translations of priority documents

Statement of inventorship and right  
to a grant of patent (Patents Form 7/77)Request for preliminary examination  
and search (Patents Form 9/77)Request for substantive examination  
(Patents Form 10/77)Any other documents  
(please specify)

11.

I/We request the grant of a patent on the basis of this application

Signature

*J D M Atkinson*

Date

4 March 1999

12. Name and daytime telephone number of  
person to contact in the United Kingdom

J D M Atkinson

[0113] 2444616

**Warning**

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

**Notes**

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered "Yes" Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.



-1-

## Acid-Catalysed Reactions

The present invention relates to acid-catalysed reactions for producing alkenes, ethers, acetals or ketals. Specifically the present invention relates to reactions for the formation of alkenes, ethers (including cyclic ethers), acetals and ketals in the presence of heterogeneous acid catalysts under near-critical or supercritical conditions.

In particular, the present invention seeks to provide improved acid-catalysed reactions of alcohols (whether aliphatic, aromatic or heterocyclic) to produce ethers, alkenes, acetals or ketals as required.

The use of acid catalysis in industry is widespread and of importance.

We have shown that reactions of industrial importance such as ether, acetal, ketal and alkene formation can be carried out under supercritical or near critical conditions of temperature and pressure using a heterogeneous acid catalyst with significant advantages. Their use in supercritical fluids has not previously been described.

Using supercritical fluids as a solvent eliminates the need for conventional organic solvents and hence gives environmental benefits. However, a more important consequence is that the reactions can be modified by using supercritical fluids to give surprisingly high yields and/or selectivities.

We have also found that certain products which are not easily accessible by conventional routes can be obtained more easily using the process of the present invention. Thus, whilst rearrangements may occur in conventional reactions we have found that certain reactions can be carried out under the conditions of the present invention without any significant rearrangement occurring. For example, ether formation

-2-

in supercritical fluids under the conditions of the present invention can give rise to enhanced yields of n-alkyl ethers rather than the branched products which are obtained in conventional procedures.

5

#### Ethers

Conventionally, the formation of ethers can be carried out via a wide number of classical routes e.g. Williamson Synthesis, dehydration of alcohols, alkylation of alcohols with inorganic esters, and alkylation with diazo compounds.

10

In the Williamson synthesis an alkyl halide is reacted with an alkoxide or aryloxy. This reaction therefore involves preforming the alkoxide from an alcohol by reaction with a strong base and subsequent reaction with an alkyl halide. This results in the generation of an equimolar amount of a halide salt which then must be disposed of. There are also the hazards associated with the handling of the alkyl halide in the case of volatile and/or toxic halides such as methyl iodide which is both a known carcinogen and very volatile.

15

20

In the case of reactions of alcohols with inorganic esters (e.g. the reaction of an alcohol with dimethyl sulfate), the inorganic esters are usually highly toxic. Again the alcohol has to be converted to the alkoxide using a strong base prior to the reaction. A further problem is the disposal of the aqueous effluent which can contain large amounts of inorganic salts.

25

30

The reaction of diazo compounds with alcohols is a cleaner reaction but suffers from the dangers associated with the thermal decomposition of diazo compounds. Also, diazo compounds are expensive and so it is not practicable to carry out this reaction on an industrial scale except for very high value products.

35

-3-

One of the most cost effective and atom efficient process for producing ethers is the dehydration of alcohols using an acid catalyst. This reaction is usually carried out in the liquid phase but suffers the drawback that, in the reaction of *n*-alcohols, the alcohol can rearrange from the primary to secondary and then to the tertiary carbocation, thereby giving a mixture of products. A further problem is that the use of homogeneous catalysts such as sulphuric acid require a separation or neutralisation step at the end of the process. The use of homogeneous catalysts means that these processes are usually carried out in batch or semi-batch reactors. The use of batch systems also gives increased down time for charging and discharging. There is also the disadvantage that the product will be a mixture of thermodynamic and kinetic products due to relatively long residence times in the reactor. Distillation or some other physical means of separation is therefore usually required to separate the products.

A number of other reactions are also carried out to form ethers, usually on a smaller scale, such as the reaction of a Grignard reagent with an acetal or cyclisation of alcohols with lead, silver or mercury salts all of which suffer from high cost and problems of waste disposal.

#### Acetals and Ketals

The most widely used method of formation of acetals and ketals is the reaction of alcohols with aldehydes or ketones under acidic conditions which involves the removal of water. These reactions are usually carried out in an excess of the alcohol or in an inert solvent. The conventional process therefore presents the problem of removing excess reagent and the catalyst must also be separated from the mixture if a homogenous catalyst is used.

-4-

## Alkenes

The industrial preparation of alkenes is normally carried out by dehydrogenation over noble metal catalysts or cracking reactions or dehydration reactions using inorganic acids. Such reactions present the problems of removal of catalyst, reaction solvent and distillation to purify products.

We have found that the use of supercritical fluids for the replacement of conventional solvents not only has significant environmental benefits but also leads to cleaner, higher yielding reactions.

Although the mechanism of the reactions is not fully understood it is believed that mass transport effects play a role in the observed improvements in yield and/or product selectivity. Surprisingly, the use of a heterogeneous catalyst in place of a homogeneous catalyst under near-critical or supercritical reaction conditions does not render the reaction ineffective. Instead we have found that the reactions benefit from improved yields and/or selectivity in product formation. This is so despite the expectation that the relatively severe conditions at or near the supercritical point of the reaction medium may give rise to a mixture of products because the reactants have sufficient energy to react via several different pathways.

One consequence of using the heterogeneous catalyst is that there is no need for complicated separation procedures to liberate the product from the reaction mixture and catalyst. This represents quite a benefit in terms of both the time savings and cost savings of the present invention.

We have thus found that it is possible by using a combination of supercritical fluids and a heterogeneous catalyst (e.g. the Deloxan ASP catalyst from Degussa or

-5-

Acidic Amberlyst resin from Rohm and Haas) in a continuous flow reactor to carry out a number of reactions rapidly and cleanly. These reactions can often be performed in high yield and take place under near-critical or supercritical conditions.

According to the present invention, there is provided a process in which an organic compound having the formula  $R^1CH_2OH$ ,  $R^1R^2CHOH$ , or  $R^1R^2R^3COH$  is exposed, optionally in the presence of one or more further organic compounds having the formula  $R^4CH_2OH$ ,  $R^5R^6CHOH$ ,  $R^7R^8R^9COH$  or  $R^{10}R^{11}CO$ , to a heterogenous catalyst which is able to provide a source of acid in a continuous flow reactor under supercritical or near-critical conditions with the result that an ether, acetal, ketal or alkene product is formed, wherein the conditions of temperature, pressure, and flow rate are independently controlled, and wherein each of  $R^1$  to  $R^{11}$  is independently selected from: hydrogen, hydroxyl, or an optionally substituted alkyl, alkenyl, alkynyl, aralkyl, cycloalkyl, cycloalkenyl, aryl or heterocyclic group.

Aliphatic and aromatic alcohols are preferred because they give cleaner reactions, with aliphatic alcohols being most preferred on the grounds of ease of use and lower occurrence of side products.

It is preferred that each of  $R^1$  to  $R^{11}$  when present is an alkyl group which may be optionally substituted. Since the process of the present invention is applicable to diols, triols and higher alcohols as well as alcohols, it is particularly preferred that the optional substituent, when present, on one of the groups  $R^1$  to  $R^{11}$  is hydroxyl. It is also preferable, in order to avoid the risk of unwanted side products, that the total number of alcohol groups within the organic compound does not exceed three.

When any of the  $R^1$  to  $R^{11}$  groups are optionally

-6-

substituted, the substituent groups which are optionally present may be any conventional substituent provided that any such substituent is not incompatible with alcohol functionality or with the reaction conditions.

Generally, when any of the  $R^1$  to  $R^n$  groups represents an optionally substituted alkyl group each group may independently be linear or branched and suitably contain 1 to 10, preferably 1 to 6 carbon atoms in the carbon chain, not including any optional substituent which may be present.

In relation to alkyl groups, specific examples of such optional substituents include halogen atoms and nitro, hydroxyl,  $C_{1-4}$  alkyl,  $C_{1-4}$  haloalkyl (especially  $CF_3$ ),  $C_{1-4}$  alkoxy,  $C_{1-4}$  haloalkoxy and ( $C_{1-4}$  alkoxy) carbonyl groups. Of these, hydroxyl and  $C_{1-4}$  haloalkyl are preferred. It is preferred, however, that when any of groups  $R^1$  to  $R^n$  is alkyl that the alkyl moiety is unsubstituted.

In relation to a phenyl moiety, optional substituents include halogen atoms, and nitro, hydroxyl,  $C_{1-4}$  alkyl,  $C_{1-4}$  haloalkyl (especially  $CF_3$ ) and  $C_{1-4}$  alkoxy groups.

In general, 1 to 3 optional substituents may suitably be employed. Halogen atoms when present are preferably fluorine.

Where the starting materials for the reaction may exist in isomeric form the reaction of the present invention is applicable to all such optical or geometric isomers.

Suitable catalysts include Deloxan acid catalysts (Ex. Degussa AG), zeolites, metal oxides, molecular sieves, clays, sulfonic acid derivatives, or other equivalent heterogeneous sources of a Bronsted acid (e.g. Amberlyst resin). The catalyst is ideally supported as an inert carrier. Preferably the catalyst

-7-

contains sulfonic acid groups, and more preferably the catalyst is a Deloxan catalyst or an equivalent thereof.

5 The reactions of the present invention are carried out in a single homogeneous phase. However, in reactions where water is generated this may separate out as a separate phase. This separation can be helpful to the reaction. Preferably, the reactions are performed in the supercritical phase.

10 In the context of the present invention, the lower limit suitable for supporting the reaction is a condition of temperature and pressure below or near to the critical point of the solvent. When a fluid reaches its critical point its density is substantially  
15 decreased relative to its density at its boiling point at normal pressure. Small changes in pressure or temperature near the critical point cause additional changes in density. The process of the present invention will operate in the fluid at temperatures and  
20 pressures below the critical point but at which the density is sufficient to ensure solvation of reagents.

The upper limit of temperature and pressure is governed only by limitations of the apparatus.

25 In practice, the choice of the near critical or supercritical fluid will depend upon the solubility of the organic compound in the fluid since a function of the supercritical or near-critical fluid is to act as a solvent for the reagents. In some cases, however, it may be particularly convenient for the near-critical or  
30 supercritical medium to be simply the alcohol itself (and the other optional reactants when present). However, the use of a separate near-critical or supercritical fluid is generally preferred.

35 Particularly favoured media include carbon dioxide, alkanes such as ethane, propane and butane, alkenes, and saturated halocarbons such as

-8-

hydrofluorocarbons and trichlorofluoromethane.

The near-critical or supercritical reaction medium when present, may be a mixture of two or more fluids having critical points which do not require commercially unacceptable conditions of temperature and pressure in order to achieve the necessary conditions for reaction according to the present invention. For example, a mixture of carbon dioxide with an alkane such as propane may be employed close to or above the theoretical critical point of the mixture.

The alcohol starting material, if not a free-flowing liquid in its normal state may be dissolved in a solvent for the purpose of introducing the alcohol into the reactor. This solvent may be present in addition to or in place of the solvent which is to be the supercritical or near-critical reaction medium. Alternatively as stated above, the alcohol itself, and any further optional components of the reaction mixture, may be the near-critical or supercritical reaction medium.

Product formation may be monitored in-situ by means of IR spectroscopy using a suitably positioned IR cell, or by gas or liquid chromatography performed on samples drawn from the reactor periodically.

We are thus able to form ethers from primary and secondary alcohols with high conversion and good selectivity for *n*, or branched products. Surprisingly *n,n*, ethers can be formed by dehydration of *n*-alcohols with little or no rearrangement. In the case of phenolic compounds it is possible by altering the reaction conditions to favour ether formation over Friedel-Crafts alkylation and vice-versa.

We have also demonstrated that it is possible to form acetals and ketals under similar supercritical or near-critical conditions as those employed for ether formation. In the case of branched alcohols, it is also



-9-

possible to select conditions in which the corresponding alkene is obtained in high yield in preference to the ether product.

5 There is also little requirement for excess alcohols to be used in the process of the present invention because of the excellent conversion rates; this simplifies purification of the products.

10 The reactions are performed using a continuous flow reactor (preferably tubular reactor). It is therefore possible to control the residence time, and also the other reaction parameters independently. This allows greater control of the reaction resulting in more efficient and also more selective reactions than can be achieved in the conventional processes.

15 The present invention will now be described by way of example only with reference to Figure 1. Figure 1 is a schematic diagram of a continuous flow reactor according to the present invention.

20 The substrate 1, which is dissolved in an appropriate inert solvent (for example an alkane such as hexane) if it is not a free-flowing liquid or if it is a solid, is pumped into mixer 2 which is a mixing vessel. The mixer 2 may include a stirrer (not shown). However, mixing of substrate 1 and fluid 3 may equally  
25 be effected without the use of stirrer. The substrate 1 is mixed with fluid 3 which is delivered from a reservoir via a pump to mixer 2. Where required, an additional reagent can be added via the same or another pump to mixer 2 with the ratio of the reagents being  
30 independently varied as required.

The temperature and the pressure in the mixer is adjusted to a temperature and pressure close to or above the critical point of the fluid 3 as required.

35 Heating means are provided in the mixer for this purpose. The mixture is then passed into reactor 5 which contains a heterogeneous catalyst (not shown)

-10-

fixed on a suitable support. A means of controlling the pressure in the reactor is also included. The catalyst provides a source of Bronsted acid to the reaction mixture as the pressurised mixture passes over the catalyst.

After an appropriate mean residence time in reactor 5, the fluid 3, which now contains the product, is passed into pressure reduction unit 6. The products 7 are removed via a take-off tap after passing through pressure reduction unit 6. The flow rate of reactants through reactor 5 is controlled by a valve (not shown) in pressure reducer 6. Fluid 3 is vented through a relief pipe 8 for subsequent recycling or disposal.

The parameters of a typical reaction might involve a system pressure of 40-300 bar (this will of course depend on the reaction medium) and the flow rate of the reagents is typically in the range of 0.5 to 20.0 ml/min. The reactor temperature is usually in the range of 30-350°C (again this will depend on reaction medium) and the flow rate of supercritical or near critical fluid is usually in the range of 0.65 to 1.65 l/min of gaseous flow at atmospheric pressure for a 10ml reactor.

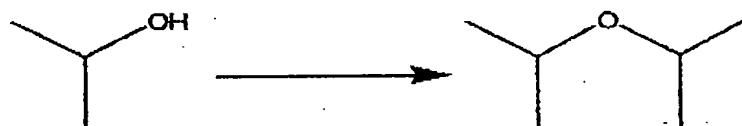
-11-

The present invention will now be illustrated by the following examples in which the temperature is the catalyst bed temperature and the solvent flow is given as gaseous flow at atmosphere pressure.

#### Example 1

##### iso-Ether Formation

Isopropyl alcohol was exposed to a Deloxan ASP 1/7 acid catalyst (available from Degussa AG) under the conditions given below in a continuous flow reactor. The volume of the reactor was 10 ml and the flow rate of the solvent was 0.65 L/min.



Temp (°C)	Pressure (Bar)	Substrate Flow Rate (ml/min)	Solvent (%)	Yield (%)
200	200	0.5	CO <sub>2</sub>	29

#### Example 2

##### n-Ether Formation

n-Butanol was exposed to an Amberlyst 15 acid catalyst under the conditions given below in a continuous flow reactor. The volume of the reactor was 20 ml and the flow rate of the solvent was 0.65 L/min.



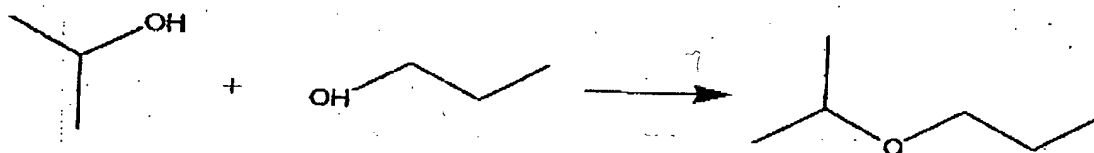
Temp (°C)	Pressure (Bar)	Substrate Flow Rate (ml/min)	Solvent (%)	Yield (%)
200°C	200	0.5	CO <sub>2</sub>	60

-12-

## Example 3

## Mixed Ether Formation

Isopropanol and *n*-propanol in the ratio of 1.2 parts isopropanol to 1.0 parts *n*-propanol were exposed to a Deloxan ASP 1/7 acid catalyst (Degussa AG) under the conditions given below in a continuous flow reactor. The reactor volume was 20 ml and the flow rate of the solvent was 0.65 L/min.



Temp (°C)	Pressure (Bar)	Substrate Flow Rate (ml/min)	Solvent (%)	Yield (%)
150	200	0.5	CO <sub>2</sub>	41

## Example 4

## Cyclic Ether

1,4-butanediol was exposed to a Deloxan ASP 1/7 acid catalyst (available from Degussa AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10ml and the solvent flow rate was 0.65 L/min.



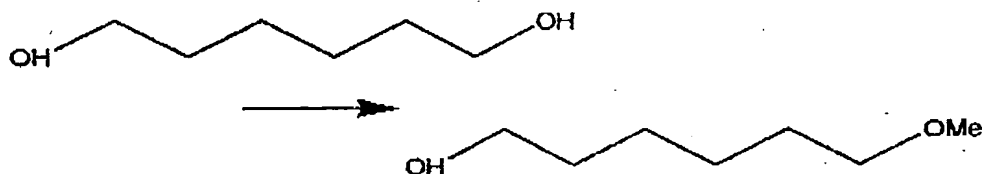
Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent	Yield (%)
200	200	0.5	CO <sub>2</sub>	100
150	100	0.5	CO <sub>2</sub>	100
125	100	0.5	CO <sub>2</sub>	87
200	100	2.0	CO <sub>2</sub>	93

-13-

### Example 5

#### Mono-Etherification of Diols

1,6-Hexanediol and methanol in the ratio of 1.0 part 1,6 hexanediol to 1.1 part methanol were exposed to a Deloxan ASP 1/7 acid catalyst (Degussa AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10 ml and the flow rate of the solvent was 0.65 L/min.

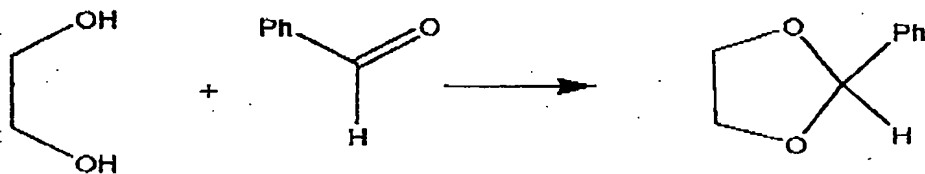


Temp(°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent (%)	Yield (%)	Di-ether (%)
100	200	0.5	CO <sub>2</sub>	32	13
200	200	0.5	CO <sub>2</sub>	65	6

### Example 6

#### Acetal Formation

1,2-Ethanedione and benzaldehyde in the ratio of 2.0 parts benzaldehyde to 1.0 part 1,2-ethanedione were exposed to a Deloxan ASP 1/7 acid catalyst (Degussa AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10 ml and the flow rate of solvent was 0.65 L/min.



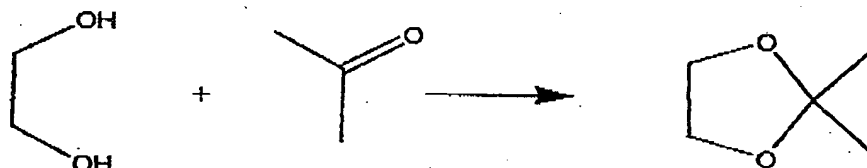
Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent (%)	Yield (%)
100	200	0.5	CO <sub>2</sub>	89
200	200	0.5	CO <sub>2</sub>	80

-14-

### Example 7

#### Ketal Formation

1,2-Ethanediol and acetone in the ratio of 2.0 parts acetone to 1.0 part 1,2 ethanediol were exposed to a Deloxan c ASP 1/7 acid catalyst (Degussa AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10 ml and the flow rate of solvent was 0.65 L/min.



Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent (%)	Yield (%)
150	200	0.5	CO <sub>2</sub>	61

### Example 8

#### Alkene Formation

2-Pentanol was exposed to a Deloxan ASP 1/7 catalyst (Degussa AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10ml and the flow rate of solvent was 0.65 L/min.



Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent (%)	Pentene (%)
200	200	0.5	CO <sub>2</sub>	100

-15-

# Claims

1. A process in which an organic compound having the formula  $R^1CH_2OH$ ,  $R^1R^2CHOH$  or  $R^1R^2R^3COH$  is exposed, optionally in the presence of one or more further organic compounds having the formulae  $R^4CH_2OH$ ,  $R^5R^6CHOH$ ,  $R^7R^8R^9COH$  or  $R^{10}R^{11}CO$ , to a heterogeneous catalyst which is able to provide a source of acid in a continuous flow reactor under supercritical or near-critical conditions with the result that an ether, acetal, ketal or alkene product is formed, wherein the conditions of temperature pressure, and flow rate are independently controlled, and wherein each of  $R^1$  to  $R^{11}$  is independently selected from: hydrogen, hydroxyl, or an optionally substituted alkyl, alkenyl, alkynyl, aralkyl, cycloalkyl, cycloalkenyl, aryl, or heterocyclic group.

2. A process according to claim 1, wherein each of  $R^1$  to  $R^{11}$  when present is an optionally substituted alkyl group, preferably each of the alkyl groups independently containing not more than 10 carbon atoms in the carbon chain (excluding optional substituents if present).

3. A process according to claim 1 or 2 wherein the total number of alcohol groups within the organic compound does not exceed three.

4. A process according to claim 1, 2 or 3, wherein the reaction is performed under supercritical conditions.

5. A process according to any preceding claim, wherein the organic compound of formula  $R^1CH_2OH$ ,  $R^1R^2CHOH$  or  $R^1R^2R^3COH$ , and optionally one or more of the compounds of formulae  $R^4CH_2OH$ ,  $R^5R^6CHOH$ ,  $R^7R^8R^9COH$  or  $R^{10}R^{11}CO$ , is dissolved in a fluid selected from: carbon dioxide, propane, an alkene, an alkyne, hydrocarbon, halocarbon, nitrogen, or a mixture of any of these.

-16-

6. A process according to claim 1, 2, 3 or 4, wherein the organic compound is the supercritical or near-critical fluid.

5 7. A process according to any preceding claim, wherein the catalyst is selected from: zeolites, metal oxides, molecular sieves, clays, or sulfonic acid derivatives.

8. A process according to claim 7, wherein the catalyst is supported on an inert carrier.

10 9. A process according to claim 7 or 8, wherein the catalyst includes a promoter.

10. A process according to any of claims 7, 8 or 9, wherein the acidity of the catalyst is provided by a sulfonic acid group.



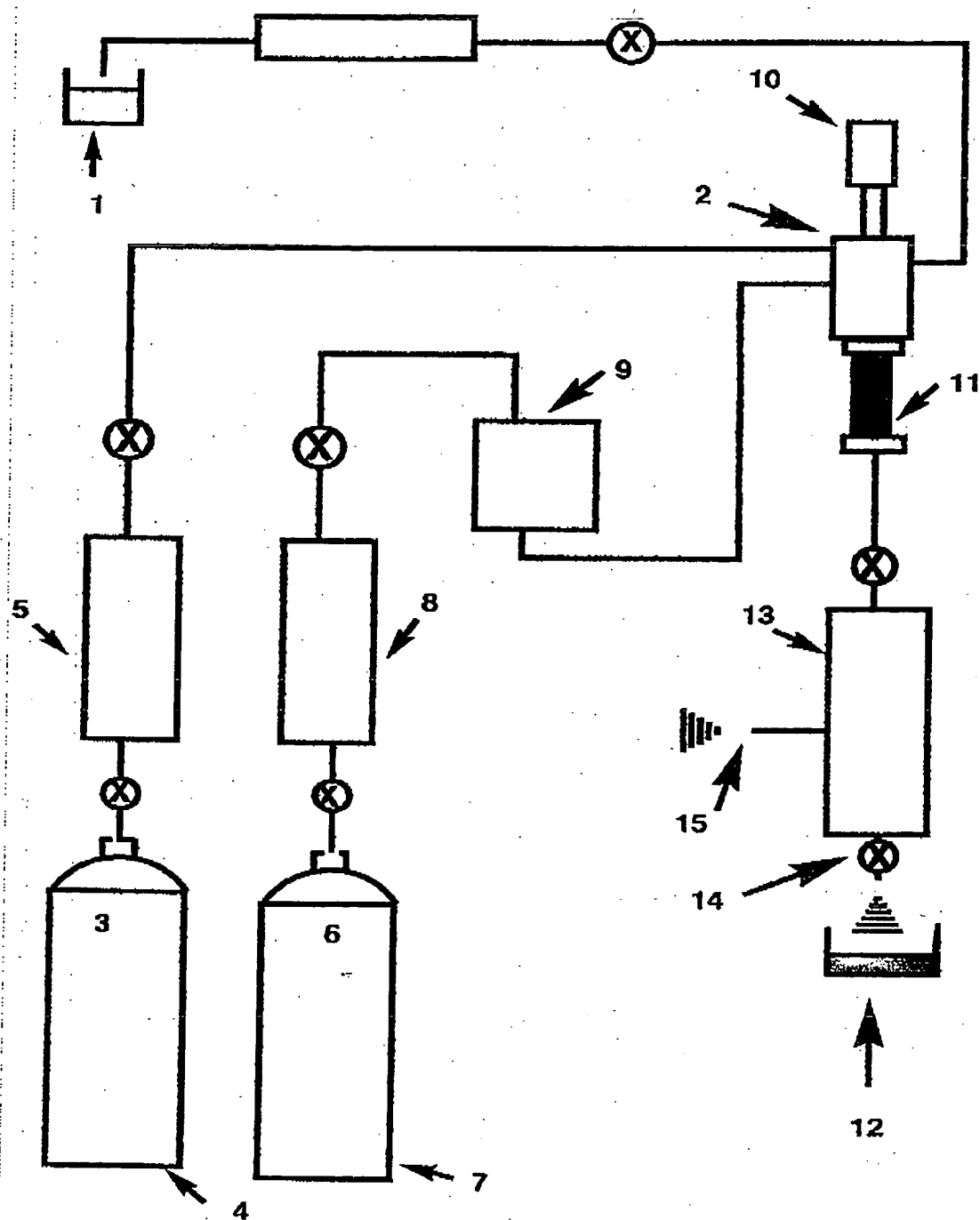
-17-

ABSTRACT

The present invention relates to acid-catalysed reactions of alcohols to produce ethers, acetals, ketals or alkenes. The reactions are carried out in the presence of a heterogenous catalyst under near-critical or supercritical conditions of temperature and pressure. The reactions of the present invention have the benefit that improved yields and/or selectivities may be obtained. In some cases, products which are not readily available by conventional acid-catalysed reactions of alcohols may be obtained.



1/1

**Figure 1**



1

2